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NINTH PROGRESS REPORT

FOR

RESEARCH INTO FUNDAMENTAL PHENOMENA ASSOCIATED WITH SPACECRAFT ELECTROCHEMICAL DEVICES — CALORIMETRY OF NICKEL-CADMIUM CELLS

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ABSTRACT

The objectives of this project are to train electrochemists in the area of battery research and to collect electrochemical and thermodynamic data of value to projects being conducted at the Goddard Space Flight Center. The specific experimental work deals with the calorimetry of Ni-Cd cells.

The work completed during the period covered by this report is subdivided into five sections.

Trickle charge experiments were conducted at 32°C on a fully charged 20 ampere-hour Ni-Cd cell. In the charge rate range of C/60 to C/80 the electrical power input approximated the heat output. At lower rates the thermal output exceeded the electrical input.

Cycling experiments on the same cell at 32°C at depths of discharge of 15% and 25% and a recharge rate of 105% gave maximum thermal outputs in the range of 0.87-0.93 and 0.90-1.13 watts respectively. In a cycling experiment at 25°C with a depth of discharge of 40% and a recharge rate of 105% the cell exhibited a maximum heat output in the range of 1.39-1.44 watts.

A computer program to process the data collected on the project has been developed and is described in detail.

Finally, a summary of the heat data collected on the 6 ampere-hour and the 20 ampere-hour cells is given.

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Research into Fundamental Phenomena Associated with Spacecraft Electrochemical Devices-Calorimetry of Nickel-Cadmium Cells

I. INTRODUCTION

The objectives of this project are

- 1) to train electrochemists in the area of battery research and
- 2) to collect electrochemical data of value to projects being conducted at the Goddard Space Flight Center.

The work completed during the period covered by this report may be subdivided into five sections. All of the experimental work deals with the 20 ampere-hour nickel-cadmium cell. The first section reports on trickle charge experiments at 32°C; the second, cycling experiments at the same temperature wherein the cell was subjected to depths-of-discharge of 15% and 25% and a recharge rate of 105%. This is followed by a cycling experiment with the same 20 ampere-hour cell at 25°C with a depth-of-discharge of 40% and a recharge rate of 105%.

A computer program to handle the data generated during these cycling experiments is described in the next section. The actual tabular data presented in this report are print-outs from the computer. Finally, a summary of the heat data collected to this point on the 6-ampere-hour and the 20-ampere-hour cells is given.

II. TRICKLE CHARGE EXPERIMENTS WITH THE 20-AMPERE-HOUR CELL AT 32°C

The 20-ampere-hour Ni-Cd cell used in these experiments and the experiments reported in the next two sections was the same for which data were reported in the Seventh Progress Report (1) and whose previous history was given in the Eighth Progress Report (2). The experimental conditions under which the trickle charge experiments were conducted were as follows:

- 1. The 20 AH cell was charged at a C/10 rate for 16 hours and discharged at a C/2 rate to a terminal voltage of 1.0 v for three consecutive times with the cell being left in the charged state in the third round.
- 2. The cell was overcharged with different trickle currents; the currents used for this study (in amperes) were 0.50, 0.33, 0.25, 0.20, 0.17, and 0.14, which correspond to rates of C/40, C/60, C/80, C/100, C/120, and C/140 respectively.
 - 3. All measurements were made at 32°C.

The data from two trickle charge experiments are given in Tables 1 and 2. The variables measured during this study were charging current, electrical power input (watts), heat out (watts), voltage and cell pressure (p.s.i.a.). The trickle charge current is also given as C/n, where n is some number and C is the capacity of the cell (20 AH). Considering this experiment as an extended overcharging of the cell, each voltage reading is a measure of the steady state condition at that particular charging rate. The open circuit voltage for the cell is 1.337 v and it is seen that at a rate of C/140 the cell voltage approaches very closely to that value.

TABLE 1. TRICKLE CHARGE EXPERIMENT AT 32°C

<u>Ra te</u>	Current (amps)	Electrical Power (in)(watts)	Heat (out)(watts)	Voltage (v)	Energy Con- version (%)	Pressure (p.s.i.a.)
C/40	0.50	0.688	0.500	1.376	72.6	18.5
C/60	0.33	0.447	0.400	1.355	89.5	16.5
C/80	0.25	0.324	0.350	1.350	108	14.3
C/100	0.20	0.269	0.300	1.347	111.7	13.5
C/120	0.17	0.228	0.230	1.342	100.9	12.5
C/140	0.14	0.187	0.225	1.340	120	12.0

Duration of experiment* (hours); C/40, 3.57; C/60, 2.33; C/80, 4.92; C/100, 3.50; C/120, 10.42; C/140, 1.0.

TABLE 2. TRICKLE CHARGE EXPERIMENT AT 32°C

Ra te	Current (amps)	Electrical Power (in)(watts)	Heat (out)(watts)	Voltage (v)	Energy Con- version(%)	Pressure (p.s.i.a.)
C/40	0.50	0.692	0.510	1.384	73.8	16.5
C/60	0.33	0.451	0.460	1.367	101.8	14.5
C/80	0.25	0.337	0.375	1.348	111.0	13.3
C/100	0.21	0.269	0.325	1.346	113.8	13.0
C/120	0.17	0.228	0.325	1.342	114.5	12.5
C/140	0.15	0.201	0.310	1.338	115.8	10.0

Duration of experiment (hours); C/40, 5.67; C/60, 14.58; C/80, 4.42; C/100, 2.33; C/120, 3.92; C/140, 4.42.

^{*} Usually a steady condition was reached in 23hours.

By comparing the two columns labeled "electrical power (put) in" and "heat (out)" in the tables it is seen that at charging rates in the range of C/60 and C/80 the watts of electrical power in becomes less than the watts of heat out, or the apparent energy conversion exceeds 100%. This relationship is shown graphically in figure 1 in which both the electrical input and the thermal output are plotted against the charging rate. The precise explanation of this observation will hopefully come as a result of a more detailed study of the cell under similar types of conditions but must be related to the self discharge of the cell. The results of a study made at 25°C as reported in table 8 of reference (1) also showed an apparent energy conversion of 100% at a rate of C/80.

Figure 2 shows the relationship between the charging rate and the cell pressure. A change in slope at currents equivalent to the C/60 and C/80 rates is apparent.

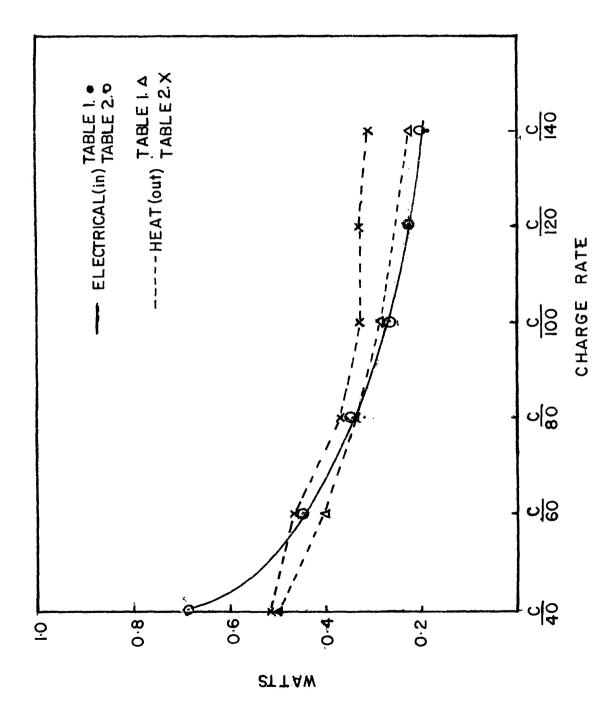


FIGURE 1. THERMAL CHARACTERISTICS OF 20 AH CELL DURING OVERCHARGE

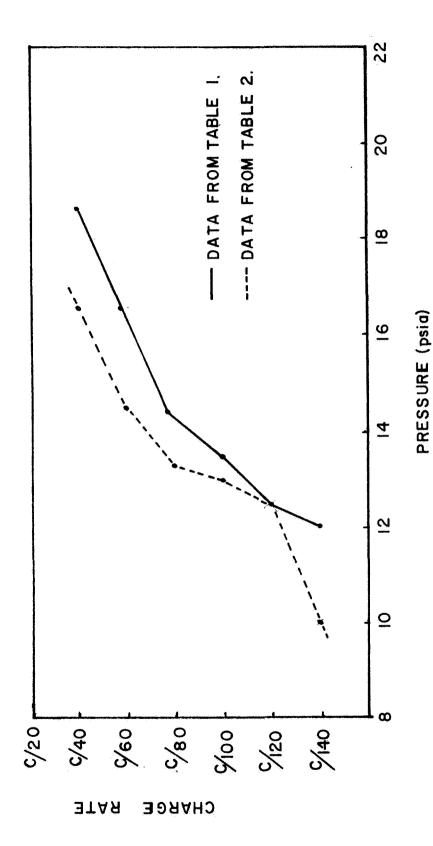


FIGURE 2. VARIATION IN CELL PRESSURE DURING TRICKLE CHARGE

III. THERMAL BEHAVIOR OF THE 20 AMPERE_HOUR NICKEL_CADMIUM CELL AT 15% AND 25% DEPTHS OF DISCHARGE AND 105% RECHARGE RATE AT 32°C

The experimental conditions were 6.00 amperes discharge current for 30 minutes and 3.15 amperes charge current for 60 minutes for the 15% depth of discharge experiment; 10.00 amperes discharge current for 30 minutes and 5.25 amperes charge current for 60 minutes for the 25% depth of discharge. Both of these experiments at 32°C used a recharge rate of 105%. The data in tables 3-6 are a representative sample of the behavior of the cell at 15% D.O.D. and 105% R.C. at 32°C. These tables are the print-outs from the computer program in a format similar to that used in previous reports. The computer program along with the meaning of the various symbols is described in section V below. The maximum heat output (QD) for the 15% D.O.D. experiment at 32°C was in the range of 0.87-0.93 watts. At this temperature the thermal behavior of the cell varies from that observed during a previous experiment at 25°C, which gave a maximum thermal output in the range of 1.45-1.58 watts under the same electrical conditions. However, this higher thermal output is out of line of other data, e.g., 25% and 40% depth experiments and is being checked. Along with the lower heat output on discharging at this temperature there is also a total absence of the characteristic endothermic heat. The apparent enthalpy (HDK or HCK) of the cell at this temperature appears to be lower than that reported at 25°C. The AH value 31.7 Kcal/eq. calculated from the 35-minute data is used to represent the enthalpy for the cell reaction during charging. The pressure within the cell during this experiment ranged from about 13.5 p.s.i.a. to about 21.0 p.s.i.a. or a change of about 7.5 p.s.i.a. during a given cycle. A pressure rise of this magnitude was not seen during the previous study at 25°C.

Table 3

1.) 30 MINUTES D.C. AT 6.00 AMPS FOR 15% D. O. D.
2.) 60 MINUTES C. AT 3.15 AMPS FOR 105% R. C. 32°C

CYCLE: 20

DIS	CHARGE							
MD	QD	VD	WD	HDW	HDK	TD	PD	JD
0	-0.54	1.34	8.040	-8.581	-32.975	84•0	21.00	150
,5	-0.67	1.32	7.920	-8.591	-33.011	83.0	20.75	187
10	-0.77	1.30	7 • 800	-8.574	-32.948	80.0	20.00	190
15	-0 • 8,5	1.29	7.740	-8.592	-33.016	76.0	19.00	183
20	-0.87	1.28	7.680	-8.558	-32.885	73.0	18.25	175
25	-0.87	1.27	7.620	-8.498	-32.655	68.0	17.00	167
30	-0.87	1.26	7.560	-8.438	-32 • 424	67.0	16.75	163
СНА	RGE							
MC	QC	VC	WC	HCW	нск	TC	PC	JC
0	-0.87	1.29	4.063	3.185	23.313	70.0	17.50	175
5	-0.74	1.34	4.220	3.472	25.413	63.0	15.75	155
10	-0.54	1.35	4.252	3.710	27.160	61.0	15.25	140
15	-0.38	1.36	4.283	3.897	28.528	58.0	14.50	130
20	-0.23	1.37	4.315	4.084	29.896	55.0	13.75	120
25	-0.15	1.38	4.346	4.193	30.695	54.0	13.50	110
30	-0.10	1.39	4.378	4.277	31.305	55.0	13.75	105
35	-0.04	1.39	4.378	4.328	31.684	56.0	14.00	100
40	-0.04	1.40	4.409	4.360	31.915	59.0	14.75	103
45	-0.10	1.41	4.441	4.340	31.766	62.0	15.50	107
50	-0.23	1.42	4.472	4.242	31.049	63.0	15.75	120
55	-0.33	1.42	4.472	4.138	30.291	73.0	18.25	140
60	-0.48	1.43	4.504	4.014	29.384	81.0	20.25	170

Table 4

1.) 30 MINUTES D.C. AT 6.00 AMPS FOR 15% D. O. D.
2.) 60 MINUTES C. AT 3.15 AMPS FOR 105% R. C. 32°C

CYCLE 25

DIS	CHARGE							
MD	QD	VD	WD	HDW	HDK	TD	PD	JD
0	-0.54	1.37	8.220	-8.761	-33.667	86.0	21.50	150
5	-0.72	1.32	7.920	-8.642	-33.210	86.0	21.50	193
10	-0.85	1.31	7.860	-8.712	-33.478	83.0	20.75	197
15	-0.90	1.29	7.740	-8.644	-33.215	76.0	19.00	187
20	-0.74	1.28	7.680	-8.428	-32.388	73.0	18.25	183
25	-0.90	1.27	7.620	-8.524	-32.754	68.0	17.00	173
30	-0.90	1.26	7.560	-8.464	-32.524	66.0	16.50	163
СНА	RGE							
МС	QC	VC	WC	HCW	нск	TC	PC	JC
0	-0.90	1.30	4.095	3.190	23.354	68.0	17.00	175
5	-0.80	1.33	4.189	3.388	24.803	62.0	15.50	160
10	-0.69	1.35	4.252	3.555	26.023	60.0	15.00	150
15	-0.46	1.36	4.283	3.820	27.960	57.0	14.25	133
20	-0.28	1.37	4.315	4.032	29.517	55.0	13.75	120
2.5	-0.17	1.38	4.346	4.167	30.506	56.0	14.00	110
30	-0.12	1.39	4.378	4.251	31.116	56.0	14.00	103
35	-0.10	1.39	4.378	4 • 277	31.305	59.0	14.75	100
40	-0.10	1.40	4.409	4.308	31.536	62.0	15.50	100
45	-0.17	1.41	4.441	4.262	31.198	67.0	16.75	105
50	-0.28	1.42	4.472	4.190	30.670	69.0	17.25	115
55	-0.41	1.42	4.472	4.060	29.722	72.0	18.00	135
60	-0.56	1.43	4.504	3.936	28.815	82.0	20.50	163

Table 5

1.) 30 MINUTES D.C. AT 6.00 AMPS FOR 15% D. O. D.
2.) 60 MINUTES C. AT 3.15 AMPS FOR 105% R. C. 32°C

CYCLE 30 DISCHARGE MD QD VD WD PD HDW HDK TD JD -0.56 0 1.36 8.159 -8.727 -33.536 81.0 140 20.25 -0.72 5 1.32 7.920 -8.642 -33.210 82.0 20.50 175 -0.85 7.800 10 1.30 -8.652 -33.247 79.0 19.75 183 -0.90 1.29 7.740 15 -8.644 -33.215 75.0 18.75 177 20 -0.90 1.28 7.680 -8.584 -32.985 72.0 18.00 170 25 -0.93 1.27 7.620 -8.550 -32.854 68.0 17.00 160 -0.93 30 1.26 7.560 -32.623 -8.490 66.0 16.50 157 CHARGE MC QC VC WC PC JC HCW HCK TC -0.93 4.095 3.164 0 1.30 23.164 66.0 16.50 165 5 -0.77 1.33 4.189 3.414 24.993 63.0 150 15.75 -0.61 10 1.35 4.252 3.633 26.592 59.0 14.75 142 15 -0.41 1.36 4.283 3.871 28.339 57.0 14.25 125 -0.25 20 1.37 4.315 4.058 29.707 55.0 13.75 115 25 -0.15 1.38 4.346 4.193 30.695 54.0 13.50 105 30 -0.10 1.39 4.378 4.277 31.305 54.0 13.50 100 -0.04 35 1.40 4.409 4.360 31.915 56.0 14.00 95 -0.10 4.409 40 1.40 4.308 31.536 69.0 17.25 97 -0.15 45 1.41 4.441 4.288 31.387 63.0 15.75 103 50 -0.25 1.42 4.472 4.216 30.859 68.0 17.00 115

4.092

3.988

29.953

29.194

73.0

83.0

18.25

20.75

135

170

4.504

4.504

55

60

-0.41

-0.51

1.43

1.43

Table 6

1.) 30 MINUTES D.C. AT 6.00 AMPS FOR 15% D. O. D.
2.) 60 MINUTES C. AT 3.15 AMPS FOR 105% R. C. 32°C

CYCLE 35 DISCHARGE PD MD QD VD WD HDW HDK TD JD 0 -0.51 1.34 8.040 -8 - 555 -32.875 84.0 21.00 150 -33.011 5 -0.67 1.32 7.920 -8.591 84.0 21.00 185 -0.77 7.800 -8.574 -32.948 81.0 20.25 10 1.30 187 15 -0.85 1.29 7.740 -8.592 -33.016 77.0 19.25 180 20 -0.87 7.680 -8.558 -32.885 73.0 18.25 175 1.28 25 -0.87 1.27 7.620 -8.498 -32.655 63.0 15.75 165 30 7.560 -32.424 67.0 16.75 164 -0.87 1.26 -8.438 CHARGE MC VC WC HCK TC PC JC QC HCW -0.87 16.75 1.29 4.063 3.185 23.313 67.0 170 4.189 5 15.75 -0.85 1.33 3.337 24.424 63.0 155 10 -0.72 1.34 4.220 3.498 25.603 61.0 15.25 140 15 -0.51 1.35 4.252 3.736 27.350 57.0 14.25 125 20 -0.33 1.36 4.283 3.949 28.907 55.0 13.75 115 25 -0.20 1.37 4.315 4.110 30.086 55.0 13.75 105 30 -0.10 1.38 4.346 4.245 31.075 55.0 13.75 95 4.328 35 -0.04 1.39 4.378 31.684 55.0 13.75 94 40 -0.04 1.40 4.409 4.360 31.915 57.0 14.25 95 45 -0.10 4.441 4.340 31.766 62.0 1.41 15.50 100

4.216

4.009

3.962

30.859

29.343

29.005

66.0

73.0

81.0

16.50

18.25

20.25

115

130

163

4.472

4.472

4.504

50

55

60

-0.25

-0.46

-0.54

1.42

1.42

1.43

Tables 7-10 present the data collected during the 25% D.O.D. experiment at 32°C. The maximum heat output during discharging varied in the range of 0.90-1.13 watts for the sample cycles taken for these tables. In contrast to the performance during the 15% D.O.D. the cell during the 25% D.O.D. exhibits both an exothermic and the endothermic characteristic. The endothermic part of the thermal cycle appears after about 25 minutes of charging and remains until the end of the charging cycle. This endothermic portion is considerable, e.g., 0.49 watts. The thermal behavior during this cycle is at variance with previous experiments in that the heat did not swing to the exothermic side toward the end of the charging cycle. A further deviation from the accepted behavior is the poor precision of the observed heat in the same time in the cycle. For example, the 55 minute QC values from tables 7-10 are 0.31, 0.23, 0.36, and 0.49 watts respectively. The statistical analysis to be conducted will better describe the precision and accuracy of the data but it would appear that the cell at this point was acting erratically.

The apparent enthalpy during charging (33.9-34.7 Kcal/eq. is slightly greater than the theoretical value of 33.6 Kcal/eq. This is an indication of the presence of secondary exothermic reactions during the charging. The pressure change within the cell during a given cycle of the experiment was usually less than 3.5 p.s.i.a., much less than that observed during the previous 15% experiment. A precise comparison of the data in tables 7-10 and previous 25% D.O.D. experiments can not be made because of the difference in the extent of recharge; 105% during this experiment and 110% during the previous experiment.

Table 7

1.) 30 MINUTES D.C. AT 10.00 AMPS FOR 25% D. O. D.
2.) 60 MINUTES C. AT 5.25 AMPS FOR 105% R. C. 32°C

CYCLE 18

DIS	CHARGE							
MD	QD	VD .	WD	HDW	HDK	TD	PD	JD
0	0.20	1.41	14.100	-13.890	-32.025	50.0	12.50	55
5	-0.17	1.29	12.900	-13.079	-30.154	48.0	12.00	95
10	-0.51	1.28	12.800	-13.315	-30.699	47.0	11.75	95
15	-0.72	1.26	12.600	-13.322	-30.716	45.0	11.25	90
20	-0.82	1.25	12.500	-13.326	-30.724	44.0	11.00	85
25	-0.85	1.23	12.299	-13.152	-30.323	42.0	10.50	80
30	-0.90	1.22	12.199	-13.104	-30.212	42.0	10.50	73
CHA	RGE							
МС	QC	vc	wc	HCW	нск	T.C	PC	JC
0	-0.90	1.22	6.404	5.500	24.156	42.0	10.50	100
5	-0.85	1.31	6.877	6.025	26.459	41.0	10.25	79
10	-0.56	1.33	6.982	6 • 414	28.171	40.0	10.00	57
15	-0.30	1.34	7.034	6.726	29.539	40.0	10.00	60
20	-0.04	1.35	7.087	7.037	30.907	39•0	9.75	53
25	0.13	1.36	7.140	7.271	31.934	39.0	9.75	45
30	0.26	1.37	7.192	7.453	32.733	39.0	9.75	43
35	0.31	1.38	7.244	7.558	33.191	40.0	10.00	4.2
40	0.31	1.39	7.297	7.610	33.422	41.0	10.25	43
45	0.36	1.39	7.297	7.662	33.649	42.0	10.50	47
50	0.36	1.40	7.349	7.714	33.880	44.0	11.00	57
55	0.31	1.41	7.402	7.715	33.883	45.0	11.25	75
60	0.20	1.41	7.402	7.611	33.428	53.0	13.25	83

Table 8

1.) 30 MINUTES D.C. AT 10.00 AMPS FOR 25% D. O. D.
2.) 60 MINUTES C. AT 5.25 AMPS FOR 105% R. C. 32 C

CYCLE 20

DIS	CHARGE							
MD	QD	VD	WD	HDW	HDK	TD	PD	JD
0	0.10	1.33	13.300	-13.194	-30.419	49.0	12.25	65
5	-0.25	1.30	13.000	-13.256	-30.563	47.0	11.75	97
10	-0.61	1.27	12.700	-13.319	-30.708	46.0	11.50	93
15	-0.82	1.26	12.600	-13.426	-30.955	45.0	11.25	85
20	-0.90	1.24	12.399	-13.304	-30.673	43.0	10.75	81
25	-0.98	1.23	12.299	-13.281	-30.621	42.0	10.50	75
30	-1.00	1.22	12.199	-13.207	-30.451	41.0	10.25	73
СНА	RGE							
МС	QC	VC	WC	HCW	нск	TC	PC	JC
0	-1.00	1.28	6.720	5.712	25.085	41.0	10.25	100
5	-0.93	1.31	6.877	5.947	26.118	42.0	10.50	75
10	-0.64	1.33	6.982	6.337	27.830	40.0	10.00	65
15	-0.36	1.34	7.034	6.674	29.312	40.0	10.00	55
20	-0.12	1.36	7.140	7.012	30.796	39.0	9.75	50
25	0.05	1.37	7.192	7.246	31.823	39.0	9.75	45
30	0.20	1.37	7.192	7.401	32.505	40.0	10.00	43
35	0.33	1.38	7.244	7.583	33.305	40.0	10.00	41
40	0.39	1.39	7.297	7.688	33.763	41.0	10.25	43
45	0.39	1.40	7.349	7.740	33.993	43.0	10.75	50
50	0.36	1.40	7.349	7.714	33.880	45.0	11.25	60
55	0.23	1.41	7.402	7.637	33.541	47.0	11.75	75
6.0	0.10	1.41	7.402	7.508	32.973	51.0	12.75	97

1.) 30 MINUTES D.C. AT 10.00 AMPS FOR 25% D. O. D.
2.) 60 MINUTES C. AT 5.25 AMPS FOR 105% R. C. 32°C

Table 9

CYCLE 23

DIS	CHARGE							
MD	QD	VD	WD	HDW	HDK	TD	PD	JD
0	0.20	1.34	13.399	-13.190	-30.411	42.0	10.50	60
5	-0.12	1.29	12.900	-13.027	-30.034	47.0	11.75	85
10	-0.48	1.27	12.700	-13.189	-30.409	46.0	11.50	85
15	-0.69	1.26	12.600	-13.296	-30.656	44.0	11.00	80
20	-0.82	1.24	12.399	-13.226	-30.494	42.0	10.50	75
25	-0.85	1.23	12.299	-13.152	-30.323	41.0	10.25	67
30	-0.90	1.22	12.199	-13.104	-30.212	41.0	10.25	60
СНА	RGE							
МС	QC	VC	wc	HCW	нск	TC	PC	٦c
0	-0.90	1.28	6.720	5.815	25.540	41.0	10.25	90
5	-0.85	1.31	6.877	6.025	26.459	41.0	10.25	67
10	-0.56	1.33	6.982	6.414	28.171	40.0	10.00	60
15	-0.36	1.34	7.034	6.674	29.312	40.0	10.00	53
20	-0.10	1.32	6.930	6.828	29.988	39.0	9.75	47
25	0.05	1.36	7.140	7.194	31.592	39.0	9.75	43
30	0.26	1.37	7.192	7.453	32.733	39.0	9.75	40
35	0.36	1.38	7.244	7.609	33.418	39.0	9.75	40
40	0.44	1.39	7.297	7.740	33.990	4.0 • 0	10.00	40
45	0.46	1.39	7.297	7.765	34.104	41.0	10.25	45
50	0.41	1.40	7.349	7.766	34.107	43.0	10.75	55
55	0.36	1.41	7.402	7.767	34.110	46.0	11.50	70
60	0.20	1.41	7.402	7.611	33.428	50.0	12.50	93

Table 10

1.) 30 MINUTES D.C. AT 10.00 AMPS FOR 25% D. O. D.
2.) 60 MINUTES C. AT 5.25 AMPS FOR 105% R. C. 32°C

CYCLE 24

DIS	CHARGE							
MD	QD	VD	WD	HDW	HDK	TD	PD	٥٦
0	-0.02	1.34	13.399	-13.423	-30.948	48.0	12.00	50
5	-0.30	1.29	12.900	-13.208	-30.452	47.0	11.75	87
10	-0.67	1.28	12.800	-13.471	-31.058	46.0	11.50	87
15	-0.90	1.26	12.600	-13.504	-31.134	45.0	11.25	83
20	-1.03	1.24	12.399	-13.433	-30.971	42.0	10.50	75
25	-1.11	1.23	12.299	-13.411	-30.920	41.0	10.25	70
30	-1.13	1.22	12.199	-13.337	-30.749	40.0	10.00	65
СНА	RGE							
МС	QC	VC	WC	HCW	нск	TC	PC	JC
0	-1.13	1.26	6.615	5 • 477	24.055	40.0	10.00	90
5	-1.08	1.31	6.877	5.792	25.435	4:00	10.00	70
10	-0.82	1.33	6.982	6.156	27.034	40.0	10.00	60
15	-0.51	1.34	7.034	6.519	28.629	39.0	9.75	55
20	-0.25	1.35	7.087	6.830	29.997	39.0	9.75	47
25	-0.04	1.36	7.140	7.090	31.138	39.0	9.75	43
30	0.13	1.37	7.192	7.324	32.164	40.0	10.00	40
35	0.28	1.38	7.244	7.532	33.077	40.0	10.00	39
40	0.36	1.38	7.244	7.609	33.418	41.0	10.25	40
45	0.46	1.39	7.297	7.765	34.104	42.0	10.50	47
50	0.49	1.46	7.664	8.159	35.832	43.0	10.75	5 7
55	0.49	1.41	7.402	7.896	34.679	46.0	11.50	73
60	0.49	1.41	7.402	7.896	34.679	50.0	12.50	100

IV. THERMAL BEHAVIOR OF 20 AMPERE_HOUR NICKEL_ CADMIUM CELL AT 40% DEPTH OF DISCHARGE AND 105% RECHARGE RATE AT 25°C

The last in a series of studies of the 20 AH Ni-Cd cell at 25°C involved a 40% depth of discharge experiment. The cycle included a discharge at 16.0 amperes for 30 minutes and a charge at 8.4 amperes for 60 minutes equivalent to 40% depth of discharge and 105% recharge. The cell used in this series of experiments was the Gulton Industries type VO-20 HS AD Ni-Cd cell serial No. 233 described in references (1) and (2).

Tables 11-14 present typical data collected during the 40% D.O.D. experiment. The data were taken from cycles 17, 18, 19 and 20 in a total of 22 cycles. The maximum heat output (QD) during the discharge process for this set of 40% D.O.D. experiments was in the range of 1.39-1.44 watts considering the 5-minute lag in heat recording. The previous experiments at 15% and 25% depths of discharge at 25°C produced 1.45-1.58 watts and 1.25 watts respectively.

The steady state that is reached during the charging of the cell appears at 20 to 35 minutes if the pressure is taken as the measure of the steady state. The pressure characteristic of the cell during this experiment seems to follow in a general way those of the cell established during both the 15% and 25% depth of discharge experiments. The pressure reaches its minimum value in about 20 minutes, increases slightly up to 45 min., at which time it begins a very rapid rise for the remainder of the cycle. The maximum and minimum values reached during a cycle have increased from 4.50 p.s.i.a. - 7.75 p.s.i.a. for 15% and 25% D.O.D. to 6.50 p.s.i.a. - 12.50 p.s.i.a. for the 40% D.O.D. This change in residual pressure of 2.00 p.s.i.a. is not such as to indicate excessive gassing tendency of the cell. A heat output of 1.42 watts and an apparent enthalpy of 32.8 Kcal/eq. (35-minute value) indicate essentially normal behavior.

Table 11

- 1.) 30 MINUTES D.C. AT 16.00 AMPS FOR 40% D. O. D.
- 2.) 60 MINUTES C. AT 8.40 AMPS FOR 105% R. C. 25°C

CYCLE 17

DIS	CHARGE							
MD	QD	VD	WD	HDW	HDK	TD	PD	JD
0	-0.23	1.33	21.280	-21.510	-30.996	40.0	10.00	105
5	-0.59	1.28	20•480	-21.073	-30.366	48.0	12.00	160
10	-0.98	1.26	20.160	-21.141	-30.464	45.0	11.25	153
15	-1.21	1.24	19.840	-21.054	-30.339	43.0	10.75	147
20	-1.29	1.22	19.520	-20.812	-29.990	40.0	10.00	133
25	-1.34	1.21	19.360	-20.704	-29.834	39.0	9.75	115
30	-1.39	1.19	19.040	-20.436	-29.447	37.0	9.25	103
СНА	RGE							
MC	QC	VC	WC	HCW	нск	TC	PC	JC
0	-1.39	1.27	10.668	9.271	25.447	37.0	9.25	130
5	-1.34	1.32	11.087	9.743	26.742	36.0	9.00	107
10	-1.05	1.34	11.256	10.196	27.986	34.0	8.50	85
15	-0.69	1.36	11.423	10.726	29.442	32.0	8.00	70
20	-0.41	1.37	11.507	11.095	30.454	30.0	7.50	57
25	-0.15	1.38	11.591	11.438	31.396	27.0	6.75	50
30	0.05	1.39	11.675	11.730	32.195	27.0	6.75	45
35	0.20	1.40	11.759	11.969	32.852	27.0	6.75	43
40	0.26	1.41	11.843	12.105	33.225	28.0	7.00	45
45	0.26	1.42	11.927	12.189	33.455	29.0	7.25	55
50	0.15	1.42	11.927	12.085	33.171	30.0	7.50	73
55	-0.04	1.43	12.011	.11.962	32.833	34.0	8.50	97
60	-0.25	1.44	12.095	11.839	32.495	48.0	12.00	150

Table 12

- 1.) 30 MINUTES D.C. AT 16.00 AMPS FOR 40% D. O. D.
 2.) 60 MINUTES C. AT 8.40 AMPS FOR 105% R. C. 25° C
 - CYCLE 18

DIS	CHARGE							
MD	QD	VD	WD	HDW	HDK	TD	PD	JD
0	-0.28	1.32	21.120	-21.402	-30.840	42.0	10.50	105
5	-0.67	1.27	20.320	-20.991	-30.247	46.0	11.50	163
10	-1.03	1.25	20.000	-21.033	-30.308	44.0	11.00	153
15	-1.21	1.24	19.840	-21.054	-30.339	42.0	10.50	147
20	-1.31	1.22	19.520	-20.838	-30.027	40.0	10.00	135
25	-1.34	1.20	19.200	-20.544	-29.603	37.0	9.25	117
30	-1.39	1.19	19.040	-20.436	-29.447	32.0	8.00	103
СНА	RGE							
MC	QC	VC	WC	HCW	нск	T _i C	PÇ	JC
0	-1.44	1.28	10.752	9.303	25.536	32.0	8.00	130
5	-1.39	1.32	11.087	9.691	26.600	31.0	7.75	105
10	-1.11	1.34	11.256	10.144	27.843	29.0	7.25	8,3
15	-0.72	1.36	11.423	10.701	29.371	28.0	7.00	65
20	-0.41	1.37	11.507	11.095	30.454	27.0	6.75	55
25	-0.10	1.38	11.591	11.490	31.538	27.0	6.75	5.0
30	0.05	1.39	11.675	11.730	32.195	27.0	6.75	45
35	0.18	1.40	11.759	11.943	32.781	28.0	7.00	4.3
40	0.26	1.41	11.843	12.105	33.225	28.0	7.00	47
45	0.26	1.41	11.843	12.105	33.225	30.0	7.50	57
50	0.15	1.42	11.927	12.085	33.171	32.0	8.00	75
55	-0.02	1.44	12.095	12.072	33.135	36.0	9.00	103
60	-0.23	1.44	12.095	11.865	32.566	48.0	12.00	150

Table 13

1.) 30 MINUTES D.C. AT 16.00 AMPS FOR 40% D. O. D.

2.) 60 MINUTES C. AT 8.40 AMPS FOR 105% R. C. 25°C

CYCLE 19

DIS	CHARGE							
MD	QD	VD	WD	HDW	HDK	TD	PD	JD
0	-0.28	1.36	21.760	-22.042	-31.762	40.0	10.00	95
5	-0.64	1.27	20.320	-20.965	-30.210	45.0	11.25	150
10	-1.00	1.25	20.000	-21.007	-30.271	44.0	11.00	147
15	-0.67	1.24	19.840	-20.511	-29.555	42.0	10.50	143
20	-1.31	1.22	19.520	-20.838	-30.027	40.0	10.00	1,27
25	-1.37	1.20	19.200	-20.570	-29.641	37.0	9.25	113
30	-1.39	1.18	18.880	-20.276	-29.217	37.0	9.25	100
CHÀ	RGE							
MC	QC	V.C	WC	HCW	нск	TC	PC	JC
0	-1.39	1.28	10.752	9.355	25.678	37.0	9.25	127
5	-1.37	1.32	11.087	9.717	26.671	35.0	8.75	105
10	-1.08	1.34	11.256	10.170	27.914	30.0	7.50	80
15	-0.72	1.35	11.340	10.617	29.140	28.0	7.00	65
20	-0.41	1.37	11.507	11.095	30.454	27.0	6.75	55
25	-0.15	1.38	11.591	11.438	31.396	27.0	6.75	47
30	0.08	1.39	11.675	11.755	32.266	28.0	7.00	43
35	0.20	1.40	11.759	11.969	32.852	29.0	7.25	43
40	0.23	1.41	11.843	12.079	33.154	32.0	8.00	45
45	0.26	1.41	11.843	12.105	33.225	36.0	9.00	55
50	0.18	1.42	11.927	12.111	33.242	38.0	9.50	75
55	-0.04	1.43	12.011	11.962	32.833	48.0	12.00	105
60	-0.33	1.44	12.095	11.761	32.282	0.0	0.00	160

Table 14

1.) 30 MINUTES D.C. AT 16.00 AMPS FOR 40% D. O. D.
2.) 60 MINUTES C. AT 8.40 AMPS FOR 105% R. C. 25°C

CYCLE 20

DIS	CHARGE							
MD	QD	VD	WD	HDW	HDK	TD	PD	JD
0	-0.23	1.33	21.280	-21.510	-30.996	42.0	10.50	120
5	-0.61	1.28	20•480	-21.099	-30.403	49.0	12.25	165
10	-1.00	1.25	20.000	-21.007	-30.271	45.0	11.25	160
15	-1.18	1.24	19.840	-21.029	-30.302	43.0	10.75	153
20	-1.29	1.22	19.520	-20.812	-29.990	41.0	10.25	140
25	-1.37	1.21	19.360	-20.730	-29.871	38.0	9.50	120
30	-1.39	1.18	18.880	-20.276	-29.217	36.0	9.00	105
СНА	RGÉ							
MC	QC	VC	WC	HCW	нск	TC	PC	JC
0	-1.42	1.27	10.668	9.245	25.376	38.0	9.50	130
5	-1.37	1.32	11.087	9.717	26.671	35.0	8.75	110
10	-1.08	1.34	11.256	10.170	27.914	30.00	7.50	80
15	-0.72	1.35	11.340	10.617	29.140	28.0	7.00	70
20	-0.38	1.37	11.507	11.121	30.525	27.0	6.75	60
25	-0.10	1.38	11.591	11.490	31.538	26.0	6.50	50
30	0.10	1.39	11.675	11.781	32.337	26.0	6.50	45
35	0.23	1.40	11.759	11.995	32.923	26.0	6.50	45
4.0	0.31	1.41	11.843	12.157	33.367	28.0	7.00	50
45	0.31	1.42	11.927	12.241	33.598	29.0	7.25	60
50	0.20	1.43	12.011	12.221	33.544	31.0	7.75	73
55	0.05	1 • 44	12.095	12.150	33.348	36.0	9.00	105
60	-0.10	1.45	12.179	12.078	33.152	50.0	12.50	160

V. THE COMPUTER PROGRAM

The computer program described below has a threefold purpose.

- 1. To facilitate the calculations required during the treatment of the data collected during the battery cycling experiments.
 - 2. To provide an optimum format for the tabulated data, and
- 3. To expedite the investigator by the rapid assimilation of the data.

The program is written in level E Fortran IV language primarily for use in the IBM 1130 computer. The IBM 1130 computer is a third generation digital computer composed of

- 1. The 1442 card reader and punch,
- 2. The 1132 printer,
- 3. The 1134 paper tape reader.
- 4. The central processor with 8000 words of core and
- 5. One 2315 disk with 512,000 word storage capacity. Version 2 of the IBM 1130 Disk Monitor System was used for the program below.

The main line program consists of two nested DO loops with two function subprograms called under the names of QD and QC respectively. The logic of the program is given in the Flow Charts of NICDD, QD, QC. The name given to the main routine is NICDD which stands for Ni-Cd Data. Considering the format used to report the data published in previous reports, the program was written in two parts, the charge part and the discharge part. The calculations performed on the discharge and charge data are put into separate DO loops and nested so as to run over one complete cycle of discharge and charge. The function subprograms QD, and QC are used to convert the heat reading in millivolts to watts by way of the heater calibration curve. QD does the above calculation for the discharge data

and QC does the same for the charge data.

The shorthand symbols used in the program have the following meaning:

- XD the heat output in millivolts during discharge
- QD the heat output in watts during discharge
- VD the voltage of the cell during discharge
- HDW the apparent enthalpy of the cell during discharge in watts
 - HDK the apparent enthalpy of the cell during discharge in Kcal/eq.
 - TD the transducer reading during discharge in millivolts
 - PD the transducer reading during discharge in p.s.i.a.
 - JD the adhydrode reading during discharge in millivolts

The symbols XC, QC, VC, HCW, HCK, TC, PC, and JC are the same as the variables above except they refer to data collected during charging.

```
*IOCS CARD, 1132PRINTER, DISK
*ONE WORD INTEGERS
*NAME NICDD
      REAL KOL
                                    VD(7,10), WD(7,10), HDW(7,10),
      DIMENSION MD(7
                       ) ,
     1HDK(7,10),TD(7,10),PD(7,10),JD(7,10),MC(13
                                                     ) •
     1VC(13,10),WC(13,10),HCW(13,10),HCK(13,10),TC(13,10),PC(13,10),
     1JC(13,10)
      COMMON XD(7,10),XC(13,10)
      DATA MD/0.5.10.15.20.25.30/
      DATA MC/0,5,10,15,20,25,30,35,40,45,50,55,60/
      N = 7
      DO 27 J = 1.0
      WRITE (3.4)
    4 FORMAT ('1','1.) 30 MINUTES D.C. AT 16.00 AMPS FOR 40/ D. O. D.')
      WRITE (3,1)
    1 FORMAT ('0','2.) 60 MINUTES C. AT 8.40 AMPS FOR 105/ R. C. 32 C')
      WRITE(3 ,7) J
    7 FORMAT ('0' + 20X + 'CYCLE' + 12)
    MD IS TIME 5 MIN. INTERVALS DURING DISCHARGE
C
    XD IS THE HEAT OUTPUT IN MILLIVOLTES DURING DISCHARGE
C
C
    VD IS THE VOLTAGE OF THE CELL DURING DISCHARGE
C
    WD IS THE INPUT ENERGY IN WATTS DURING DISCHARGE
C
    HDW IS THE APPARENT ENTHALPY OF THE CELL IN WATTS DURING DISCHARGE
C
    HDK IS THE APPARENT ENTHALPY DURING DISCHARGE GIVEN IN KCALS.
C
    TD IS THE TRANDUCER READING DURING DISCHARGE IN MV.
    PD IS THE PRESSURE WITHIN THE CELL DURING DISCHARGE
    JD IS THE ADHYDRODE SIGNAL DURING DISCHARGE IN MV.
      READ(2.5)(XD(1.J).I=1.7)
    5 FORMAT (7F6.2)
      READ (2,6)(VD(I,J),I=1,7)
    6 FORMAT (7F6.2)
      READ (2,20)(TD(I,J),I=1,7)
      READ(2,21)(JD(I,J),I=1,7)
   20 FORMAT (7F4.1)
   21 FORMAT(714)
      WRITE (3,25)
   25 FORMAT ( '0', 'DISCHARGE')
      WRITE (3,11)
   11 FORMAT ('0'+1X+'MD'+3X+'QD'+4X+'VD'+6X+'WD'+7X+'HDW'+6X+'HDK'+5X+
     1'TD',4X, 'PD',4X, 'JD')
      CD = 16
      F = 96487 \cdot 0
      CONV = 4185.0
C
    CALCULATION OF THE VARIABLES WD. HDW. HDK. AND PD
      DO 10 I = 1.7
      WD(I+J) = VD(I+J) * CD
      (L_{\bullet}I)DW - (L_{\bullet}I)DD = (L_{\bullet}I)WDH
      X = F / (CONV * CD)
      HDK(I \rightarrow J) = HDW(I \rightarrow J) + X
      B = 0.25
  CALIBRATION CURVE FOR THE CONVERSION OF MV. TO P.S.I.A.
      PD(I,J) = B * TD(I,J)
      K = QD(I,J)
```

```
10 WRITE (3,9) MD(I ), K
                                   •VD(I,J),WD(I,J), +DW(I,J), +DK(I,J),
     1TD(I,J),PD(I,J),JD(I,J)
    9 FORMAT( 00 + 12 + 2x + F5 + 2 + 2x + F4 + 2 + 2x + F7 + 3 + 2x + F7 + 3 + 2x + F7 + 3 + 2x + F4 + 1 + 2x +
     1F5.2.2X.13)
    MC,XC,VC,WC,HCW,HCK,TC, AND JC ARE THE SAME VARIABLES AS ABOVE FOR
    THE CHARGE CONDITIONS
      READ (2,14)(XC(I,J),I=1,13)
   14 FORMAT (13F6.2)
      READ (2,15)(VC(I,J),I=1,13)
   15 FORMAT(13F6.2)
      READ(2,22)(TC(1,J),I=1,13)
      READ (2,23)(JC(I,J),I=1,13)
   22 FORMAT(13F4.1)
   23 FORMAT(1314)
      WRITE (3,16)
   16 FORMAT ('0', CHARGE')
      WRITE (3,17)
   17 FORMAT('0',1X,'MC',3X,'QC',4X'VC',6X,'WC',7X,'HCW',6X,'HCK',4X'TC'
     1, 4X, PC', 4X, JC')
      CC = 8.4
      F =96487.0
      CONV =4185.0
    CALCULATION OF THE VARIABLES WC. HCW. HCK. AND PC
C
      DO 18 I = 1.13
      OO * (L(I)OV = (L(I)OW)
      (LeI)DW + (LeI)DD = (LeI)WDH
      X = F / (CONV * CC)
      HCK(I,J) = HCW(I,J) * X
   CALIBRATION CURVE FOR THE CONVERSION OF MV. TO P.S.I.A.
      PC(I_{\bullet}J) = B * TC(I_{\bullet}J)
      L = QC(I,J)
   18 WRITE(3,19) MC(I ), L
                                    • VC(I•J) • WC(I•J) • HCW(I•J) • HCK(I•J) •
     1TC([,J),PC([,J),JC([,J)
   19 FORMAT('0',12,2X,F5,2,2X,F4,2,2X,F7,3,2X,F7,3,2X,F7,3,2X,F7,3,2X,F4,1,2X,
     1F5.2,2X,13)
   27 CONTINUE
      STOP
      END
*STORE
             WS UA
                     NICDD
*ONE WORD INTEGERS
      REAL FUNCTION QD(I,J)
      COMMON XD(7,10), ZD(13,10)
   FUNCTION SUBPROGRAM TO CONVERT MILLIVOLT SIGNAL TO HEAT IN WATTS.
C THE Y INTERCEPT OF THE HEATER CALIBRATION CURVE.
      D = 0.080
C THE SLOPE OF THE HEATER CALIBRATION CURVE.
      E = 0.0259
      QD
               = E * XD(I_{\bullet}J) + D
      RETURN
      END
*STORE
                      QD.
             WS UA
*ONE WORD INTEGERS
      REAL FUNCTION QC(I,J)
      COMMON ZC(7,10), XC(13,10)
   FUNCTION SUBPROGRAM TO CONVERT MILLIVOLT SIGNAL TO HEAT IN WATTS.
```

```
C THE Y INTERCEPT OF THE HEATER CALIBRATION CURVE.

D = 0.080

C THE SLOPE OF THE HEATER CALIBRATION CURVE.

E = 0.0259

QC = E * XC(I,J) + D

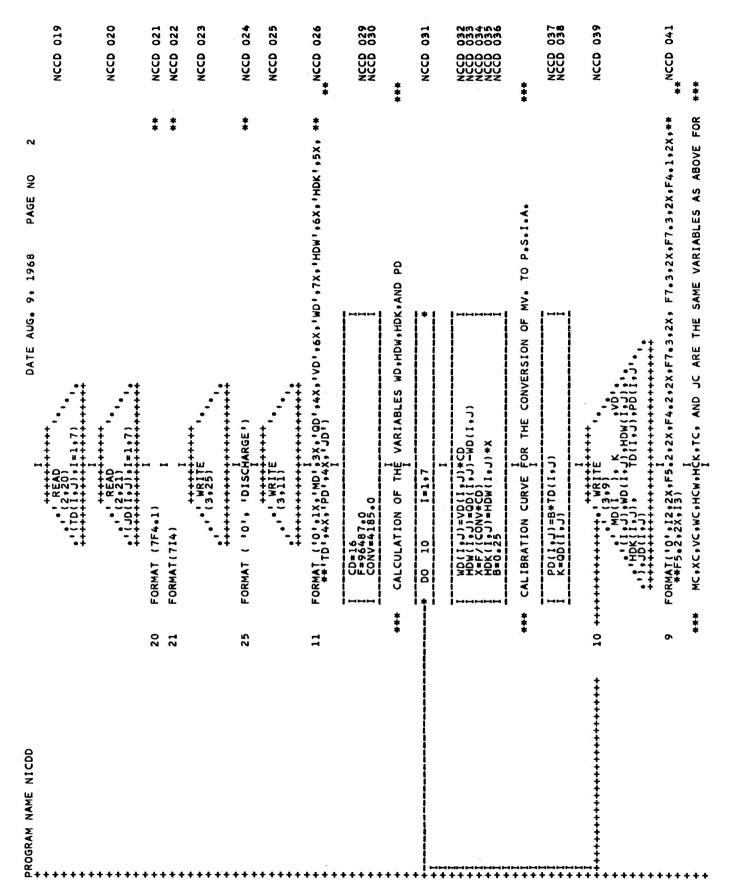
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VI. SUMMARY OF THERMAL CHARACTERISTICS OF NICKEL-CADMIUM CELLS

A brief summary of the thermal characteristics of the 6 ampere-hour and 20 ampere-hour nickel-cadmium cells as measured on this project is given in table 15.

The 6 ampere-hour cell exhibits a trend toward increased heat with increased depth of discharge. This trend is also observed with the 20 ampere-hour cell with the exception of the single value for the 15% depth experiment. This experiment is being checked. The series F value of 4.0 watts at a depth of discharge of 25% is not in accord with any other observation and is believed to be due to the erratic behavior of the particular cell. It is not considered representative of the normal behavior of a nickel-cadmium cell of this capacity. The few experiments run at the elevated temperature of 32°C indicate that the heat output is actually less than for the corresponding experiment at 25°C. The difference is small and additional experiments at several more temperatures would be required before any definitive statement could be made regarding the heat of activation for the process.

TABLE 15. SUMMARY OF THERMAL CHARACTERISTICS OF NICKEL_CADMIUM CELLS

Six Ampere-Hour Cells

Series	Date	Tempera- ture (°C)	Depth of Discharge (%)	Charge Rate (%)	Maximum Heat Output (watts)	Maximum Endothermic Heat (watts)
A	7-66	25	25	110	- 0.58	+0.10
В	8 - 66	25 25	25 15	114	-0.32	+0.08
C	8 - 66	25	25	114	-0.60	+0.10
D	10-66	25	40	110	-1.14	+0.15

			Twenty	Ampere-Hou	r Cells		
Ϊà	4,6-68	25	15	105	-1.58	+0,23	
Ib	4,6-68	25	25	110	-1.25	+0.07	
H	1,3-68	25	25	113*	-1.30	+0.07	
G	7,9-67	25	25	105	-1.20	+0.13	
F	7,9-67	25	25	105	-4.00	-	
Ja	7,9-68	25	40	105	-1.44	+0.26	
Jъ	7,9-68	32	15	105	-0.93	-	
Jc	7,9-68	32 ,	25	105	-1.13	+0.49	

^{*} Corrected for 62-minute charge in Series H.

VII. FUTURE WORK

From a comparison of the thermal data collected on the 20 amperehour nickel-cadmium cell it is obvious that only the results obtained
at a 15% depth of discharge at 25°C are out of line with other experiments.
This experiment will be checked.

All of the experiments to this point have investigated the thermal behavior of Gulton Ni-Cd cells equipped with third control electrodes.

It is intended to investigate the thermal characteristics of a General Electric 20 ampere-hour cell with the same electrical specifications.

VIII. REFERENCES

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- 2. R. T. Foley and G. D. Mitchell, Eighth Progress Report on Contract No. NAS 5-10105, April 1, 1968 June 30, 1968.

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